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THE EFFECT OF Cu DOPING AND MAGNETIC FIELD ON SPECIFIC HEAT OF $La_{0.50}Ca_{0.50}MnO_3$

Y.E.Gunanto[1], B.Kurniawan[1], W.Nursiyanto[2], H.Tanaka[3], T.Ono[3], A.Purwanto[4], W.A. Adi[4] and S.Poertadji[1]

[1]Faculty of Education, Universitas Pelita Harapan, Karawaci, Tangerang,15811
[2]Faculty of Informational Technic, Universitas Multi Media Nusantara, Tangerang
[3]Department of Physics, Tokyo Institute of Technology Tokyo 152-8551, Japan
[4]Centre of Technology for Nuclear Industrial Materials (PTBIN) - BATAN Kawasan Puspiptek Serpong, Tangerang, 15341
e-mail: ye_gunanto@yahoo.com

ABSTRACT

THE EFFECT OF Cu DOPING AND MAGNETIC FIELD ON SPECIFIC HEAT OF $La_{0.50}Ca_{0.50}MnO_3$. We report specific heat measurements of $La_{0.50}Ca_{0.50}Mn_{1-y}Cu_yO_3$ for y = 0.05, 0.15, 0.20 without and with applied magnetic field up to 9 T. In all cases, the external magnetic field does not influence the specific heat. At the temperature range of 100-270 K, as the Cu dopant is increased, the specific heat decreases. We found that at a range of 3-20 K, the specific heat contains terms proportional to T and T^3, but a $T^{3/2}$ term is not appear. The Debye temperature is 365 K for all samples indicating that the Cu-doping is not influencing the lattice factor β.

Key words: Specific heat, Cu doping, Debye temperature

ABSTRAK

PENGARUH PENDOPINGAN Cu DAN MEDAN MAGNET PADA PANAS JENIS $La_{0.50}Ca_{0.50}MnO_3$. Telah dilakukan pengukuran panas jenis $La_{0.50}Ca_{0.50}Mn_{1-y}Cu_yO_3$ untuk y = 0,05; 0,15; 0,20 tanpa medan magnet dan dengan medan magnet hingga 9 T. Dalam semua kasus, medan magnet luar tidak mempengaruhi panas jenis. Pada rentang suhu 100 K hingga 270 K, jika Cu *dopant* bertambah, maka panas jenis akan berkurang. Pada rentang suhu 3 K hingga 20 K diperoleh bahwa besar panas jenis hanya memenuhi fungsi T dan T^3, sedang fungsi $T^{3/2}$ tidak tampak. Untuk semua sampel mempunyai suhu *Debye* 365 K, ini mengindikasikan bahwa *doping* Cu tidak mempengaruhi faktor kisi β.

Kata kunci: Panas jenis, *Doping* Cu, Suhu *Debye*

INTRODUCTION

The mixed-valent perovskite manganese oxides of ABO_3-type structure ($R_{1-x}A_xMnO_3$: R = La, Pr, Nd; A = Ca, Sr, Ba) have attracted considerable attention because of their unusual magnetic and electronic properties [1-8]. The half-doped manganites, with $x = 0.5$ are charge-spin-orbital ordered [11-12]. Charge, spin, and lattice interactions appear to play a significant role in determining these properties. At certain doping levels (x) a real space ordering of charge carriers has been observed at low temperatures [9-10]. This charge-ordered state can be destroyed by a modest external magnetic field [11-12]. The spin are antialigned between Cu $e_{g\downarrow}$ and Mn $e_{g\uparrow}$, which makes carrier hopping cost more energy then to flip the carrier spins [13].

Previously, for measurement of low-temperature specific heat of lanthanum-manganites $La_{0.67}Ba_{0.33}MnO_3$ and $La_{0.8}Ca_{0.2}MnO_3$, J.J.Hamilton *et al* [14] found that the temperature dependence has an electronic linear term and lattice cubic term. The specific heat and found that $La_{0.5}Ca_{0.5}MnO_3$ is in the charge-ordered state accompanied by AFM ordering at T < 140 K [15]. A magnetic field is sufficient to induce the transition state from insulating AFM to metallic FM in $La_{0.5}Ca_{0.5}MnO_3$ [16]

Another interesting phenomenon has shown by the ABO_3-type structure, i.e. the high Debye temperatures that often found in this compounds. For example, in $LaNiO_3$ was found that the Debye temperature θ_D = 400 ± 20 K [17]. L.Ghiveldar *et al* [18] found θ_D = 348 K and 368 K for Pb-doped and Ca-doped respectively. D.Vershey *et al* [19] found the θ_D for perovskites manganite is around 350-450 K.

In this study, we report effect of replacing Mn with Cu on the specific heat, the density of state at the Fermi level $N(E_F)$, and the Debye temperature θ_D of the $La_{0.5}Ca_{0.5}Mn_{1-y}Cu_yO_3$ with $0.05 \leq y \leq 0.20$.

EXPERIMENTAL METHOD

Polycrystalline samples of $La_{0.5}Ca_{0.5}Mn_{1-x}Cu_xO_3$ with x = 0.05, 0.15 and 0.20 were prepared by a solid-state reaction method from a stoichiometric mixture of La_2O_3, $CaCO_3$, MnO_2 and CuO with purity more than 99%. Compound were mixed thoroughly in the high energy milling HEM for 10 hours, then heated at 1350 °C for 6 hours. The process was repeated with HEM for 5 hours and heated at 1100 °C for 24 hours to obtain the single-phase compound. The phase purities of the powdered samples were checked using X-Ray diffraction measured at room temperature using X-Ray Diffractometer Philips PW 1710 ABD 3520, and the data was analyzed using the RIETAN program [20]. The data analysis results reveal that all samples prepared are single phase with orthorhombic structure, and space group of Pnma.

The specific heat was measured in the temperature range of 1.8-300 K in the magnetic field with the range of 0- 9 T using the SQUID Quantum Design at Tanaka Lab. Titech Tokyo.

RESULTS AND DISCUSSION

In Figure 1 we show the specific heat C as a function of temperature, T for three samples with different Cu dopant. We considered a temperature dependence of the form Equation (1)

$$C = \gamma T + \delta T^{3/2} + \beta T^3 \quad \text{..... (1)}$$

where:

γ, δ, and β are constants

These three terms are expected to arise respectively from charge carriers, ferromagnetic spin wave, and lattice. For low-temperature, the specific heat show the same pattern, but for temperature of 100-270 K, with increasing Cu doping, the specific heat C decreased.

Figure 2 and Figure 3 show that the external magnetic field are not influencing the patterns nor the value of specific heat C. In Figure 4 the specific heat data is shown in the form of C/T vs. T^2. The linearity of the curves above ~ 3 K indicates that the data fit Equation (1) very well with the value of δ = 0, for the magnetic field H = 0 T. So the value of β and γ can be provided as gradient and the point of cross section

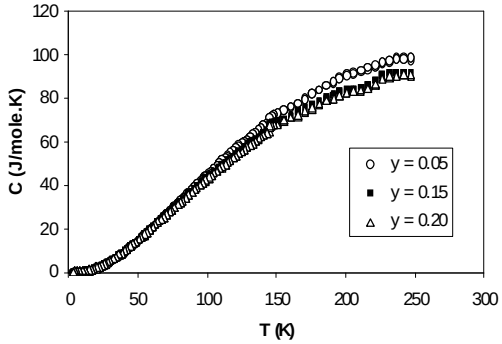

Figure 1. Specific heat versus temperature plot of $La_{0.5}Ca_{0.5}Mn_{1-y}Cu_yO_3$ with y = 0.05; 0.15, and 0.20 at H = 0 T.

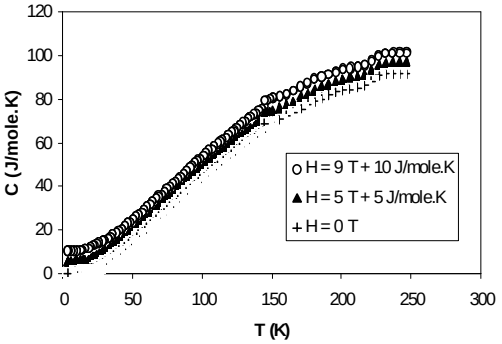

Figure 2. Specific heat versus temperature plot of $La_{0.5}Ca_{0.5}Mn_{0.85}Cu_{0.15}O_3$ with H = 0 T, 5 T and 9 T.

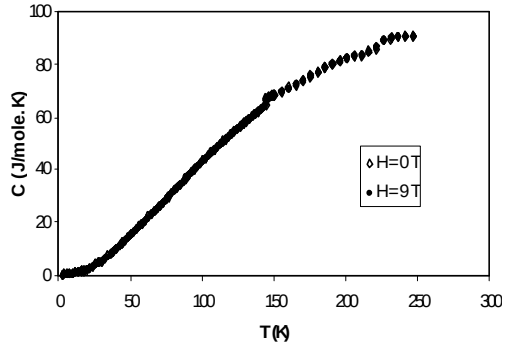

Figure 3. Specific heat versus temperature plot of $La_{0.5}Ca_{0.5}Mn_{0.80}Cu_{0.20}O_3$ with H = 0 T and 9 T.

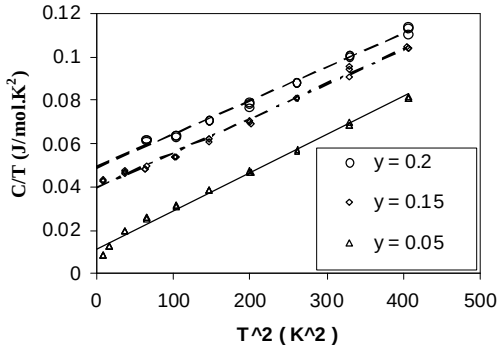

Figure 4. The plot of as C/T versus T^2 at magnetic field H=0.Lines are best fits to the form $C = \gamma T + \beta T^3$.

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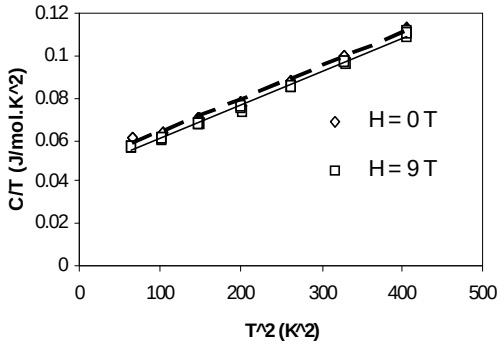

Figure 5. The plot of C/T versus T^2 for Cu = 0.20. Lines are best fits to the form $C = \gamma T + \beta T^3$.

at C/T axis, respectively. At low temperature the amplitude of spin wave is small and consequently the interaction among waves is negligible [21] and therefore $\delta = 0$.

From Figure 4 and Figure 5, we obtain β values 0.2 mJ/mol.K^4 for all samples. Using the standard expression for Debye Temperature at Equation (2).

$$\theta_D = \left(\frac{12\pi^4 pR}{5\beta} \right)^{1/3} \quad \text{.....} \quad (2)$$

Where:

R = Ideal gas constant
p = 5 is the number of atoms per formula unit
θ_D = 365 K for all samples

As a complement of the measurement of $R_{1-x}A_xMn_{1-y}Cu_yO_3$ samples, this study has confirmed the high Debye temperature of this type of structure. For external magnetic field H = 0 T, the values of γ are 14 mJ/mol.K^2, 39 mJ/mol.K^2 and 49 mJ/mol.K^2 for Cu-dopant 0.05, 0.15, and 0.20 respectively. If the linear term in specific heat arises entirely from the presence of the charge carries[19], then the density of state $N(E)$ at the Fermi energy $E = E_F$ is given by Equation (3)

$$\gamma = \frac{\pi^2}{3} k_B^2 N(E_F) \quad \text{.....} \quad (3)$$

Where:

k_B = Boltzmann's constant

$N(E_F)$ = 3.52x10^{24}/eV.mol; 1.01x10^{25}/eV.mol, and 1.24x10^{25}/eV.mol respectively for y = 0.05, 0.15 and 0.20.

Increasing the magnetic field relatively unchanged the γ value (see Table 1). γ value represent the number of charge carriers, that reason to the insensitive to the external magnetic field. As comparisons, some measurement results of $R_{1-x}A_xMn_{1-y}Cu_yO_3$ samples are shown at the Table 1.

As shown at the Table 1, we observed that the γ value and therefore the number of charge carriers $N(E_F)$ increase in the presence of Cu. This parameter continued increasing when the Cu-dopant concentration increased. This observation conform to the fact that the Fermi energy level for Cu is lower than that for Mn, the reason that the free-electron value for γ in Cu is higher than in Mn. Table 1 also shown that lattice factor β values are relatively unchanged for all samples and are not affected by the presence of Cu nor the external magnetic field. This implies that the specific heat is insensitive to the magnetic field for all samples

CONCLUSION

The specific heat for all samples is insensitive to the external magnetic field up to 9T. The presence of external magnetic field is not influencing values for samples with and without Cu doping. Upon increasing the Cu dopant, the γ and therefore the charge carriers increase and results in decreasing specific heat values at high temperature range.

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Table 1. Some result of measurement of $R_{1-x}A_xMn_{1-y}Cu_yO_3$ samples

Sample	x	y	γ(mJ/mol.K^2)	β(mJ/mol.K^4)	θ_D (K)	N(E_F)(/mol.eV)	Reference
$La_{0.67}Ba_{0.33}MnO_3$	0.33	0	4.4±0.1	0.13±0.005	383±2	(1.12±0.02)x10^{24}	J.J.Hamilton *et al*
			5.6±0.15	0.173±0.005	416±2	(1.41±0.04)x10^{24}	
$La_{0.8}Ca_{0.2}MnO_3$	0.2	0	7.8±0.07	0.164±0.0015	390±1	(2.0±0.02)x10^{24}	
$La_{0.9}Ca_{0.1}MnO_3$	0.1	0	4.7	-	368	-	L.Ghiveldar *et al*
$La_{0.78}Pb_{0.22}MnO_3$	0.22	0	15	0.23	348	3.8x10^{24}	
$La_{0.9}Ca_{0.1}MnO_3$	0.1	0	-	0.168	387	-	D.Varshey *et al*
$La_{0.8}Ca_{0.2}MnO_3$	0.2	0	2.16	0.141	410	-	
$La_{0.67}Ca_{0.33}MnO_3$	0.33	0	1.96	0.139	412	-	
$La_{0.5}Ca_{0.5}Mn_{0.95}Cu_{0.05}O_3$	0.5	0.05	14	0.2	365	3.52x10^{24}	This study
$La_{0.5}Ca_{0.5}Mn_{0.85}Cu_{0.15}O_3$	0.5	0.15	39	0.2	365	1.01x10^{25}	
$La_{0.5}Ca_{0.5}Mn_{0.80}Cu_{0.20}O_3$	0.5	0.20	49	0.2	365	1.24x10^{25}	H = 0 T
$La_{0.5}Ca_{0.5}Mn_{0.85}Cu_{0.15}O_3$	0.5	0.15	34	0.2	365		H = 9 T
$La_{0.5}Ca_{0.5}Mn_{0.80}Cu_{0.20}O_3$	0.5	0.20	47	0.2	365		

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